

# CANADA

## THE PATENT OFFICE

PATENT No. 465,495

ISSUED MAY 30, 1950

### Stabilization of Colouring Compositions Containing Diazonium Salts

Hans Z. Lecher, Plainfield, New Jersey, U.S.A., and  
William B. Hardy, and Frederic H. Adams,  
Bound Brook, New Jersey, U.S.A., assignors to  
American Cyanamid Company, New York, New  
York, U.S.A.

Application January 29, 1943, Serial No. 499,409

In the United States April 1, 1942

No drawing

1

This invention relates to compositions containing ice colour diazo components, diazotized or undiazotized and to methods of preventing the thinning of printing pastes containing such diazotized components.

Producing prints in colours on various vegetable fibres often is effected by padding the goods with an alkaline solution of an azoic coupling component and printing with a printing paste containing diazotized ice colour diazo components either freshly prepared or in the form of stabilized diazonium salts. This is a well-known cheap process for producing azoic prints and requires no difficult treatment. However, it is open to a very serious disadvantage. The printing pastes containing the diazonium salt stabilized or unstabilized do not keep well and particularly tend to thin out rapidly losing their desired printing consistency. It is with this thinning action that the present invention is concerned.

According to the present invention the diazonium salt, either in stabilized form or freshly prepared, is associated with a water-soluble sulphonie acid containing at least one olefinic double bond or acetylenic triple bond.

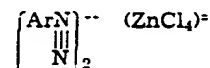
When an aromatic amine is diazotized in acid solution, a diazonium salt is formed which is generally assumed to have the following formula:



where Ar stands for the aromatic radical of the diazo component and X stands for the anion of the acid. These diazonium salts are salts of the very strong diazonium bases and the aqueous solutions contain essentially the diazonium cations and the anions of the acid used, as indicated by the formula. Some of these diazonium salts are difficult to isolate because of their great solubility. Others are not so soluble and can be easily isolated. Some are difficult to handle after isolation because of their explosivity, others are rather stable and do not represent an explosive hazard. It is also known that if the anion of the acid X<sup>-</sup> is properly chosen, in almost all cases diazonium salts of lower solubility may be produced and therefore isolated, and it is also known that many of these diazonium salts have lost their explosive character and can be stored and handled in the dry state without danger;

2

this kind of diazonium salt is sometimes referred to as "stabilized" diazonium salts. They comprise such compounds as certain aromatic sulphonates, without olefinic double bonds, borofluorides; and particularly salts of complex acids sometimes referred to as double salts, the most important of them being the double salts of diazonium chlorides and zinc chloride which correspond to the formula:



It should be borne in mind that also these "stabilized" diazonium salts including the above-mentioned double salts are true diazonium salts, i.e., the aqueous solution contains the same diazonium cations as the solution of any other diazonium salt derived from the same base. The present invention deals with inhibiting the thinning action of diazonium salts only, and not with any similar action that might be observed with other types of diazo compounds.

While it is not intended to limit the present invention to any theory of action we believe that it is highly probable that lowering of viscosity of printing gums is essentially caused by the diazonium cation because the same kind of thing results regardless of the anion of the diazonium salt and even the double salts of the stabilized diazonium salts described above exert a similar thinning action. Presumably in aqueous solution the stabilized diazonium salts are ionized to give the same diazonium cation. The pH of the printing paste is not critical so long as it is on the acid side for the present invention does not deal with any other types of pastes. Alkaline medium as is well known causes rearrangement of the diazonium salts to diazo compounds of different structure.

While not desiring to limit the invention thereto, we believe that the evidence strongly indicates that the thinning action is a colloidal phenomenon rather than a chemical reaction. The following test was made: A diazonium salt derived from 2-nitro-4-methoxy aniline was added to a printing paste made up with a starch thickener; after 24 hours the then water thin solution was coupled with an alkaline solution of beta-naphthol and the azo dye formed was removed by filtration. The amount of azo dyestuff obtained indicated that the bulk of the diazonium salt was undecomposed and has reacted

9

**Example 3**

An intimate mixture is made of 100 parts of 3-nitro-4-amino anisole, 25 parts of sodium-2-methyl-2-propene-1-sulphonate of approximately 73 per cent purity, and 75 grams of sodium chloride. This mixture can be treated with mineral acid and sodium nitrite and the resulting diazo solution can then be buffered with sodium acetate and mixed with thickening gum for the production of fast colour prints on textile materials impregnated with ice colour coupling components such as arylides of 2-hydroxy-3-naphthoic acid, etc.

Printing pastes made from such mixtures have the advantage over those pastes made from the ordinary bases unblended with inhibitors in that the gums made from the blended bases retain their viscosity much longer than the other. This advantage can best be seen by consulting the following table. In this table the change of viscosity of printing pastes containing various diazos and sodium-2-methyl-2-propene-1-sulphonate as inhibitor is compared with the change of viscosity of similar pastes containing no inhibitor. In each case the base, or mixture of base with inhibitor, is treated with hydrochloric acid and sodium nitrite in the usual manner:

Base Diazotized	Parts of 73% Sodium 2-Methyl-2-Propene-1-Sulphonate Per Part Base	Inert Diluent & Parts Per Part Base	Parts Real Base in Gum	(75 Parts) Gum Used and Strength	Viscosity Reading 2 Min. After Mixing	Time of Second Viscosity Measurement After Mixing	2nd Viscosity Reading	Method of Viscosity Measurement
5-Nitro-2-Amino Anisole	0.5	Sodium Chloride 0.5	0.84	Carob Bean 2.5%	25.3	4 Hr.	13.2	A2
5-Nitro-2-Amino Anisole	0	0	0.84	Carob Bean 2.5%	22.2	4 Hr.	4.2	A2
4-Chloro-2-Nitro-Aniline	0.94	0	0.69	Carob Bean 2.5%	27.0	4 Hr.	13.5	A2
4-Chloro-2-Nitro-Aniline	0	0	0.69	Carob Bean 2.5%	24.1	4 Hr.	0.8	A2

**Example 4**

1.58 Parts of a product containing the zinc chloride double salt obtained from tetrazotized o-dianisidine corresponding to 48.8 per cent of real base and 0.215 parts of potassium 2-methyl-2-propene-1-sulphonate of 70 per cent purity are intimately mixed and dissolved in 23 parts of water and the resulting solution is thoroughly mixed with 75 parts of 2 per cent Carob Bean Gum. This viscous paste is useful for the preparation of deep blue patterns upon cellulosic material impregnated with arylides of 2-hydroxy-3-naphthoic acid, or other ice colour coupling components. The superiority of a printing paste thus made over one similarly prepared but without the sulphonate is shown by the following figures:

Printing Paste Used	Relative Viscosity Measurement After 1 Hour	Relative Viscosity Measurement After 3 1/2 Hours
Gum containing inhibitor	15.2	10.2
Same but without inhibitor	13.4	2.2

The viscosity measurements indicated above are the times in seconds for lead shot weighing 0.069 grams each to fall 130 millimetres.

**Example 5**

5.03 Parts of the zinc chloride double salt ob-

10

tained from diazotized 3-nitro-4-amino anisole corresponding to 16.7 per cent real base are mixed with 0.403 parts of the allyl ether of sodium p-phenol sulphonate. This mixture is dissolved in 21 parts of water and the resulting solution is intimately mixed with 75 parts of 2.5 per cent Carob Bean Gum. The superiority of a printing paste thus made over one similarly prepared, but without inhibitor is shown in the following table:

Printing Paste Used	Relative Viscosity Measurement After 5 Minutes	Relative Viscosity Measurement After 4 Hours
Paste containing inhibitor	60.2	29.8
Paste without inhibitor	47.0	0.7

These relative viscosity measurements are the times in seconds for copper-plated steel shot weighing 0.107 grams each to fall 130 millimetres.

**Example 6**

1.79 Parts of the zinc chloride double salt obtained from diazotized 3-nitro-4-amino anisole corresponding to 47 per cent real base are mixed with 0.35 parts of ammonium styrene beta-sul-

phonate and the resulting mixture is dissolved in a mixture of 20 parts of water and 1 part of 5N hydrochloric acid. This solution is intimately mixed with 75 parts of 2.5 per cent Carob Bean Gum. The advantage of the printing paste thus prepared over one made similarly but without the inhibitor is shown in the following table:

Printing Paste Used	Relative Viscosity After 2 Minutes	Relative Viscosity After 4 Hours
Paste containing inhibitor	153.1	43.4
Paste without inhibitor	147.3	1.0

These relative viscosity measurements are the times in seconds for spherical glass beads weighing 0.097 grams to fall 130 millimetres.

As can be seen styrene beta-sulphonate is a less effective inhibitor because of the proximity of the double bond and of the sulphonic group.

**We claim:**

Claim.—1. Compositions suitable for forming printing pastes including an azoic colour forming component included in the group consisting of diazotizable amines, diazo compositions containing water soluble diazonium salts and printing pastes containing water soluble diazonium salts derived from ice colour diazo components and a carbohydrate thickener, the colour forming com-

ponent having admixed therewith a compound belonging to the group consisting of water soluble sulphonc acids containing at least one olefinic double bond water soluble sulphonic acids containing at least one acetylenic triple bond and their water soluble salts, the compound being free from constituents capable of azoic coupling or of catalytic decomposition of the diazonium salt at room temperature, the amount of the sulphonc acid compound being sufficient to substantially inhibit thinning of the paste.

2. Diazo compositions suitable for printing containing a water-soluble diazonium salt derived from an ice colour diazo component and an effective amount of a compound belonging to the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and water-soluble sulphonic acids containing at least one acetylenic triple bond and free from groups capable of azoic coupling, and water-soluble salts of the above acids with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature.

3. A printing paste containing a carbohydrate thickener, at least one water-soluble diazonium salt derived from an ice colour diazo component and a compound included in the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and water-soluble sulphonic acids containing at least one acetylenic triple bond and free from groups capable of azoic coupling, and water-soluble salts of the above acids with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperatures, the amount of sulphonic acid compound being sufficient to substantially inhibit thinning of the paste.

4. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a compound belonging to the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and free from groups capable of azoic coupling, and their water soluble salts with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature.

5. A printing paste containing a carbohydrate thickener, at least one water-soluble diazonium salt derived from an ice colour diazo component and a compound included in the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and free from groups capable of azoic coupling, and their water-soluble salts with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature, the amount of sulphonc acid compound being sufficient to substantially inhibit thinning of the paste.

6. A composition according to claim 2 in which the diazonium salt is a diazonium chloride zinc chloride double salt.

7. A composition according to claim 4 in which the diazonium salt is a diazonium chloride zinc chloride double salt.

8. A diazotizable composition containing 3-nitro-4-amino-anisole and sufficient amount of sodium 2-methyl-2-propene-1-sulphonate to substantially inhibit the thinning of carbohydrate thickener by diazotized 3-nitro-4-amino-anisole.

9. A diazo composition comprising a water-soluble diazonium salt of diazotized 3-nitro-4-amino-anisole and a sufficient amount of sodium 2-methyl-2-propene-1-sulphonate to substantially inhibit thinning of carbohydrate printing thickener by the diazonium

salt.

10. A printing paste containing a carbohydrate thickener and water-soluble diazonium salt from diazotized 3-nitro-4-amino-anisole and sufficient amount of sodium 2-methyl-2-propene-1-sulphonate to substantially inhibit thinning of the paste.

11. The process of stabilizing printing pastes containing a carbohydrate thickener and a diazonium salt derived from an ice colour diazo component which comprises incorporating into the paste a sufficient amount of a compound belonging to the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and water-soluble sulphonic acids containing at least one acetylenic triple bond and free from groups capable of azoic coupling, and water-soluble salts of the above acids with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature, to substantially inhibit thinning of the paste by the diazonium salt.

12. The process of stabilizing printing pastes containing a carbohydrate thickener and a diazonium salt derived from an ice colour diazo component which comprises incorporating into the paste a sufficient amount of a compound belonging to the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and free from groups capable of azoic coupling, and their water-soluble salts with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature, to substantially inhibit thinning of the paste by the diazonium salt.

13. A process of printing fabrics containing ice colour coupling components with a printing paste containing a carbohydrate thickener, a water-soluble diazonium salt derived from an ice colour diazo component, and a sufficient amount of a compound belonging to the group consisting of water-soluble sulphonic acids containing at least one olefinic double bond and water-soluble sulphonic acids containing at least one acetylenic triple bond and free from groups capable of azoic coupling, and water-soluble salts of the above acids with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature, to substantially inhibit thinning of the thickener by the diazonium salt.

14. A process of printing fabrics containing ice colour coupling components with a printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo component, and a sufficient amount of a compound belonging to the group consisting of water soluble sulphonic acids containing at least one olefinic double bond and free from groups capable of azoic coupling, and their water soluble salts with bases which do not couple azoically and do not catalytically decompose diazonium compounds at room temperature, to substantially inhibit thinning of the thickener by the diazonium salt.

SMART & BIGGAR.  
Victoria Bldg.,  
Ottawa, Ont.,  
Patent Agent  
of the Applicants.